

Shades of green in 15th century paintings: combined microanalysis of the materials using synchrotron radiation XRD, FTIR and XRF

Nati Salvadó · Salvador Butí · Marine Cotte ·
Gianfelice Cinque · Trinitat Pradell

Received: 19 July 2012 / Accepted: 27 November 2012 / Published online: 8 December 2012
© Springer-Verlag Berlin Heidelberg 2012

Abstract A representative selection of green paintings from fifteenth century Catalonia and the Crown of Aragon are analyzed by a combination of synchrotron radiation micro-analytical techniques including FTIR, XRD, and XRF. The green pigments themselves are found to be a mixture of copper acetates/basic copper acetates and basic copper chlorides. Nevertheless, a broader range of green shades were obtained by mixing the green pigment with yellow, white, and blue pigments and applied forming a sequence of micrometric layers. Besides the nature of the pigments themselves, degradation and reaction products, such as carboxylates, formates and oxalates were also identified. Some of the copper based compounds, such as the basic copper chloride, may be either part of the original pigment or a weathering product. The high resolution, high brilliance, and small

footprint of synchrotron radiation proved to be essential for the analysis of those submillimetric paint layers made of a large variety of compounds heterogeneous in nature and distribution and present in extremely low concentrations.

1 Introduction

The characterization of the materials used by the Western European painters in fifteenth century altarpieces to obtain green shades is extremely complex. In order to obtain different green shades, the painters used mixtures of different color, including green, yellow, white and, in some cases, blue pigments, as well as various types of binders [1–4].

For the green pigments themselves, a large variety of substances, mainly copper based, were used in this period. They were obtained following several recipes using copper or copper alloys, vinegar, and in some cases, salt. The resulting compounds obtained from these recipes are a wide range of products with a similar blue-green tinge. As a consequence of exposing pieces of metal copper to acetic acid vapors in a humid environment, a series of reactions happen on the surface where copper rusts and copper acetates are formed [5–7].

If the concentration of acetic acid is decreased, a mixture of compounds between the copper acetates and the copper hydroxides in diverse proportion and levels of hydration is formed. The range of basic copper acetates produced varies between those containing none and those that have three hydroxide groups [8]. These basic copper acetates were the substances used as green pigments in the altarpieces here studied.

If in the process of manufacture of the copper pigments, chlorides are introduced—generally in the form of NaCl—basic copper (II) chlorides are also formed. Occasionally,

N. Salvadó (✉) · S. Butí
Dpt. d'Enginyeria Química, EPSEVG, Universitat Politècnica de Catalunya, Av. Víctor Balaguer s/n, 08800 Vilanova i la Geltrú, Barcelona, Spain
e-mail: nativitat.salvado@upc.edu
Fax: +34-93-8967700

M. Cotte
LAMS, Laboratoire d'Archéologie Moléculaire et Structurale, CNRS UMR8220, 3 rue Galilée, 94200 Ivry-Sur-Seine, France

M. Cotte
European Synchrotron Radiation Facility, Polygone Scientifique Louis Néel-6, rue Jules Horowitz, 38000 Grenoble, France

G. Cinque
Diamond Light Source, Harwell Campus, Chilton-Didcot, OX11 0DE Oxon, UK

T. Pradell
Dpt. Física i Enginyeria Nuclear, ESAB, Universitat Politècnica de Catalunya, Campus del Baix Llobregat, Av. del Canal Olímpic 15, 08860 Castelldefels, Barcelona, Spain

the same substances can also result from the reaction of the copper-based pigments with atmospheric contaminants [2, 5, 6].

As a consequence, the analysis of the green paint implies a great complexity. The high resolution, high brilliance, and small footprint render synchrotron radiation essential for the analysis due to the small amount, heterogeneous distribution of the materials, and the small amount of sample material available. The combination of micron sensitive analytical techniques including micro X-ray diffraction μ -XRD, micro X-ray fluorescence μ -XRF, and micro infrared spectroscopy μ -FTIR with synchrotron radiation and SEM, has shown to be a powerful tool to overcome certain limitations and to obtain more precise information on the composition and distribution of the numerous substances present.

The present study is part of a 10-year research project dedicated to the analysis of the altarpiece paintings produced in Catalonia and the Crown of Aragon during the fifteenth century [2–4, 9]. These paintings are of great quality and were sensitive to all the contemporary European influences involving either, stylistic or technical changes. Despite the great losses suffered over 500 years, an important number of altarpieces from this period—significant both in terms of quantity and quality—have been fortunately preserved. Herewith, we present a representative selection of green paint examples from the period. The variety of substances used to produce green shades is illustrated and some examples of how the alteration and aging processes modify the composition of the green paints are also presented.

Masters' painters in this small territory and during the relatively short time period—the second half of the fifteenth century—used similar materials. However, it is possible to distinguish between the materials used in the different workshops and to correlate them with the influences received, especially with regard to the greens. Besides, it is important to emphasize that this is also the period when the oil technique was introduced and progressively substituted traditional tempera.

The green samples belong to a collection of altarpieces selected to include both tempera and oil painting techniques and the different painting schools from the territory. Following these criteria, the “Sant Joan i Sant Esteve” (1455–1453) altarpiece by Honorat Borrassà¹ from the Girona School and painted with oil was selected. The altarpieces “Conestable” (1465) and “Sant Bernadí i l'Àngel Custodi” (1462–1475) by Jaume Huguet and “Sant Vicenç” (1455–1460) by Bernat Martorell belonging to the school of Barcelona both painted mainly with egg tempera were selected. Finally, “la Mare de Déu” by Pasqual Ortoneda (1459) from the school of Tarragona painted with a tempera technique where no lipids

were detected was also selected. The altarpieces by Honorat Borrassà and Bernat Martorell are on display at the MNAC (Museu Nacional d'Art de Catalunya) in Barcelona. The altarpieces by Jaume Huguet are displayed: the “Conestable” in its original location, the “Santa Àgata” chapel in the Royal Palace in Barcelona and the “Sant Bernadí i l'Àngel Custodi” in de Cathedral museum of Barcelona. Finally, the altarpiece by Pasqual Ortoneda is on display in the VINSEUM museum, in Vilafranca del Penedès, Barcelona.

2 Analytical techniques and sample preparation

Optical Microscopy (OM) and Scanning Electron Microscopy (SEM), JEOL-5600, with elemental analysis using the PCXA LINK EDS microanalyzer are used in order to obtain information of the composition, size distribution, and homogeneity of the particles in the paint samples. Small fragments or cross sections were carbon coated to ensure the electrical conductivity necessary to perform the SEM-EDS analysis.

Synchrotron-based micro X-ray diffraction (μ SR-XRD) data were obtained at Station BM16 (Spanish CRG) of the European Synchrotron Radiation Facility (ESRF, Grenoble). Small fragments cut from the samples were previously selected with the help of the optical microscope. These fragments were placed on an adhesive support from where measurements were taken in transmission geometry using a beam footprint of 30×30 microns. Thin cross sections were also prepared for some selected samples—200 microns thick. A footprint of about $20 \times 50 \mu\text{m}^2$ was found to be most adequate for the discrimination of the compounds present in the different layers. A smaller beam footprint may lead to a spotty single crystal-like X-ray diffraction pattern, dominated only by some of the big crystallites precluding the identification of the other compounds. A larger footprint hampers separation of the compounds present in the different layers. The setup included a CCD ADSC Q210r detector and 10 keV ($\lambda = 1.24 \text{ \AA}$) or 12.7 keV ($\lambda = 0.98 \text{ \AA}$) X-rays. This setup provides high sensitivity to compounds present in very low amounts and a good low angular limit adequate for some of the organic compounds present, but has some limitations in the angular resolution for highly overlapping diffraction patterns.

Synchrotron-based micro infrared spectroscopy (μ SR-FTIR) measurements were taken at the MIRIAM beamline of the Diamond Light Source [10]. On this beamline, a Bruker 80 V Fourier Transform IR Interferometer coupled with a Hyperion 3000 microscope, with a 100×100 micron area broad band, and MCT detector was used. Some μ SR-FTIR measurements were also obtained at station 11.1 of the Synchrotron Radiation Source (formerly SRS at Daresbury Laboratory). The NEXUS FTIR Spectrophotometer

¹Currently the MNAC attributes this work to the master of Sant Joan i Sant Esteve.

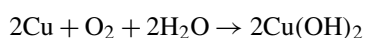
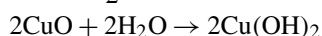
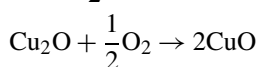
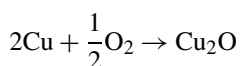
was equipped with a Nicolet Continuum microscope and MCT detector. In both cases, the spectra were obtained measuring one of the diamond windows of fresh-fractured fragments of the samples pressed in a diamond cell. Spectra were obtained in transmission mode and from different areas using a microbeam of either of 12×12 microns or 15×15 microns at the sample defined by the slits.

Synchrotron-based micro X-ray fluorescence (μ SR-XRF) measurements were taken at beamline ID21 of the European Synchrotron Radiation Facility (ESRF, Grenoble). This beamline is specialized in micro-spectroscopy in the tender X-ray domain (2–9 keV). For this experiment, the energy was fixed at 9.05 keV, using a fixed-exit Si(111) monochromator. The beam was focused down to $0.85 \mu\text{m}$ (hor.) \times $0.35 \mu\text{m}$ (ver.) using Fresnel Zone plates. Samples are raster scanned in a vertical plan, and XRF spectra are acquired on each pixel, over a 2D region, using a 80 mm^2 SDD detector (Bruker). XRF spectra are batch fitted using the PyMca software package [11].

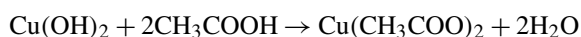
3 Results and discussion

There is quite an extensive literature on the green pigments synthesis and identification, however, the information relevant to the compounds of interest in our study appears scattered, fragmented, and often incomplete [8, 12–21]. This often hampers the identification of such compounds in historical paintings. Consequently, one of the main purposes of the paper is to give a complete account of the chemical reactions and compounds formed relevant in our study including IR and XRD data necessary for their identification. Moreover, the variety in the terminology often used to name the compounds induces some confusion.

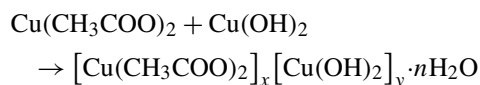
Although in theory copper metal is inert in an acid aqueous solution if oxygen is dissolved in the water, which is commonly the case when the water is in contact with the atmosphere, a series of reactions summarized in the following are produced [8]:



If acetic acid is present in the medium, copper acetate is also formed



This compound can react with the copper hydroxide producing basic copper acetates



These basic copper acetates were used as green pigments. In fact, the material obtained, as we will see is a mixture of acetates and hydroxides in variable proportions. The products we were able to determine in the altarpieces studied include the following values: $x = 1$, $y = 1$, $n = 5$; $x = 1$, $y = 3$, $n = 2$ and $x = 1$, $y = 0$, $n = 1$. The specific compounds obtained depend on the pH and the concentration of acetic acid, which can vary during the synthesis when homemade recipes are used to produce them. Increasing the concentration of acetic acid [12, 13] first $\text{Cu}(\text{CH}_3\text{COO})_2\text{Cu}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ copper II hydroxide acetate pentahydrate, then $\text{Cu}(\text{CH}_3\text{COO})_2[\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$ copper II trihydroxide acetate dihydrate and finally $\text{Cu}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}$ copper II acetate monohydrate in the form of dimmer [14] are formed [15–21].

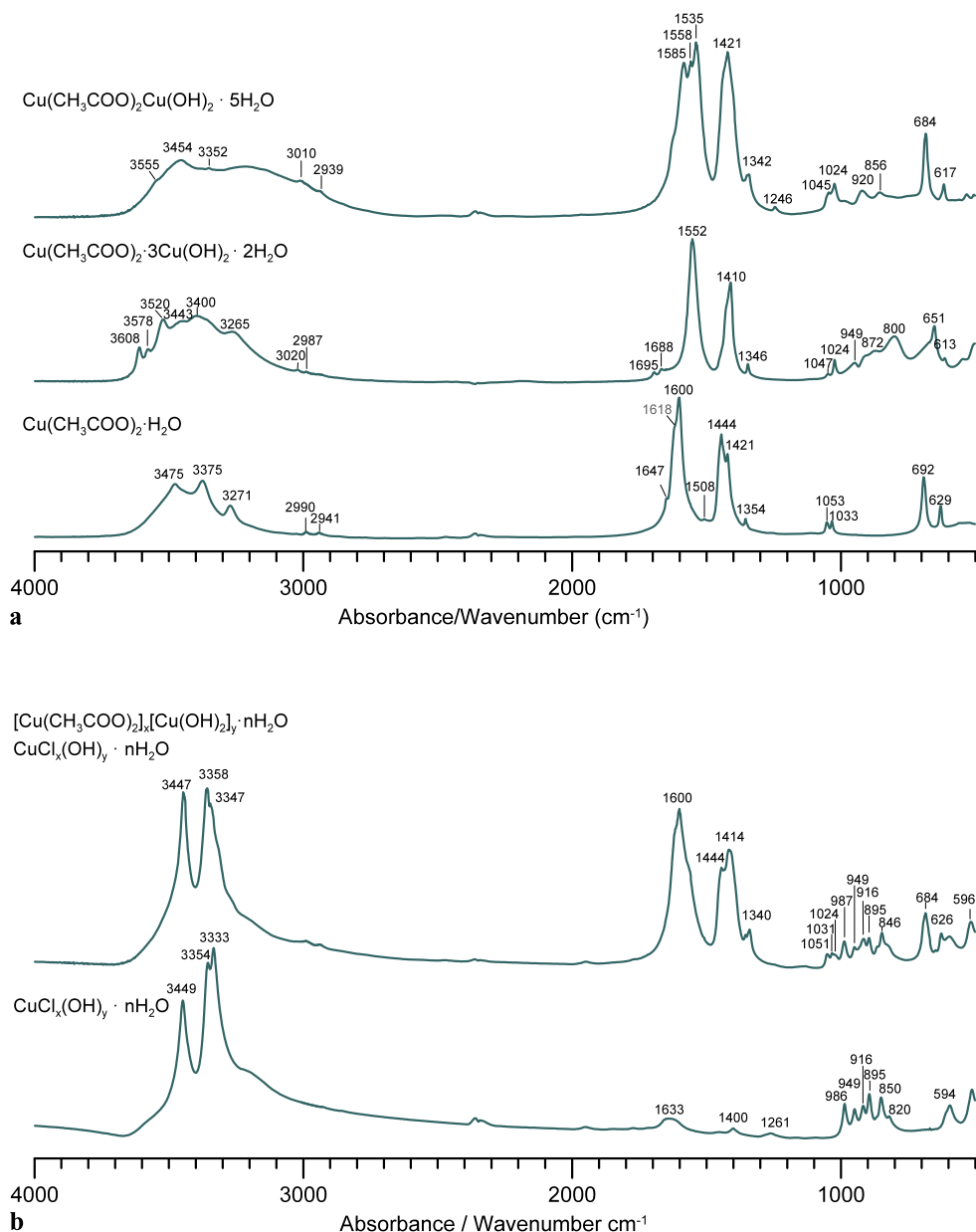
If chloride is present in the synthesis process, basic copper chlorides $[\text{CuCl}_2]_x [\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$, particularly $\text{Cu}_2\text{Cl}(\text{OH})_3$ copper II hydroxide chloride are also formed. Although the presence of those chlorides in the paint may sometimes be due to the alteration of the copper pigments, they were also obtained and used as pigments according to the recipes like those described in the manuscripts by Eracilius and Theophilus [22, 23].

The chemical reactions listed above are those relevant in the production of the substances used as green pigments in the painting of the period and geographical location under study.

IR and XRD corresponding to the compounds of interest are shown in Fig. 1 and Table 1, respectively. Figure 1a shows the IR spectra corresponding to the copper acetates/basic copper acetates $[\text{Cu}(\text{CH}_3\text{COO})_2]_x [\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$ and Fig. 1b the IR spectra corresponding to the mixture of basic copper acetates and basic copper chlorides as described in historical recipes both obtained from laboratory controlled synthesis. Table 1 gives the XRD data corresponding to all those compounds. It should be mentioned that malachite (a basic copper carbonate) often described as a green pigment used in the period, has not been found in any of the green paints analyzed, and if found it is always in very minute concentrations, and is related to the impurities present in the paint layers [3].

The paint samples are structured in submillimetric layers made of a first ground layer followed by a sequence of paint layers, and in some cases, completed by a varnish. Greens are present principally in the representation of the vegetable motifs and garments where it is also very common to find a great variation of shades. Thus, various layers of wider green shades can be found within the same sample fragment. A yellow pigment was often added to the green copper pigment to provide a different range of shades. Such yellow

Fig. 1 (a) Infrared spectra corresponding to the relevant copper acetates/basic copper acetates obtained from laboratory controlled synthesis. 128 scans, 4 cm^{-1} resolution. (b) Infrared spectra corresponding to a mixture of copper acetates/basic copper acetates and basic copper chlorides obtained by laboratory controlled synthesis following historical recipes. 128 scans, 4 cm^{-1} resolution



pigments are usually lead tin oxides, which depending on the presence or absence of silicon in the composition, are known as type II $-\text{Pb}(\text{Sn},\text{Si})\text{O}_3-$ or type I $-\text{Pb}_2\text{SnO}_4-$, respectively. Other substances related to the synthesis of the yellow pigment such as tin oxide (SnO_2 cassiterite) are also often found. A white pigment, namely lead white (usually a mixture of PbCO_3 cerussite and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ hydrocerussite in different ratios) was added for the same purpose. Both yellow and white pigments are usually present in significantly high proportion so they tenaciously mask the detection of the other materials. Furthermore, small quantities of the blue pigment azurite $-2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2-$ added to reinforce the blue shade are often found in background landscapes. Finally, when evaluating the complexity of the

composition of the samples, it is important to keep in mind the existence of reaction compounds [2] such as, carboxylates and oxalates of copper [24], lead or calcium. These compounds are formed to a more or less degree if, over the years, the metal ions from the pigments come into contact with the binding media or the environment. The tendency to produce copper carboxylates is evidenced if the binding media contains lipids [25]. Copper oxalates are also systematically found in those samples where copper carboxylates are found in large concentration near the paint surface. Finally, calcium oxalates are found on the surface and also inside cracks.

The altarpiece shown in Fig. 2a is attributed to Honorat Borrassà and was painted in the second half of the fif-

Table 1 Copper compounds identified in the paint samples

	General formula	Specific compound or mineral phase identified in the samples by SR- μ XRD	File or reference
Copper compounds related to the green pigment			
Copper acetates and basic copper acetates	$[\text{Cu}(\text{CH}_3\text{COO})_2]_x[\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$	$\text{Cu}(\text{CH}_3\text{COO})_2[\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$ $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $\text{Cu}(\text{CH}_3\text{COO})_2$	References [15, 21] JCPDS file 27-0145 JCPDS file 28-0392
Basic copper chloride	$[\text{CuCl}_2]_x[\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$	$\text{Cu}_2\text{Cl}(\text{OH})_3$	JCPDS file 70-0821 atacamite JCPDS file 25-0269 paracamite
Basic copper carbonates	$[\text{CuCO}_3]_x[\text{Cu}(\text{OH})_2]_y$	$\text{Cu}(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ $\text{Cu}_2\text{CO}_3(\text{OH})_2$	JCPDS file 15-0669 calumetite JCPDS file 72-0075 JCPDS file 83-1298 malachite
Copper compounds related to aging of the green copper pigment			
Copper carboxylates		large background: non crystalline compound	
Copper oxalates	$\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$	$\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	JCPDS file 48-1054
Copper formate and basic copper formate	$[\text{Cu}(\text{HCOO})_2]_x[\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$	non determined	

teenth century. The vegetal motifs (Fig. 2b) display a great variety of green shades. The ground layer is made of gypsum and animal glue, which is the composition of all the ground layers in all the altarpieces studied from this period and geographic area. Over the ground layer, we find a sequence of chromatic paint layers applied using drying oil as binder. The chromatic layers are shown in Fig. 2c, d and are constituted by a first layer (labelled layer 3 in Fig. 2c) of lead white, which serves as preparation over which two green layers are applied. The analyses corresponding to these green layers are shown in Fig. 3. The first green layer (labelled layer 2 in Fig. 2c, d) is a green glaze and is made of a mixture of the green pigment (and a small proportion of white pigment) with a drying oil, which gives transparency. As might be expected, copper carboxylates are detected in this layer, product of the reaction between the copper from the pigment and the free fatty acids formed as the drying oil ages. The characteristic asymmetric stretching infrared absorption band at 1587 cm^{-1} corresponding to the COO^- group is clearly determined [2] (Fig. 3a, layer 2). In the next and more external green layer (labelled layer 1 in Fig. 2c, d), the μXRF elemental distribution map reveals the presence of Sn containing particles dispersed in an homogeneous Cu matrix (Fig. 3b). The layer is an heterogeneous mixture of the copper green pigment with lead white (mixture of $\text{PbCO}_3/2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and lead-tin type I (Pb_2SnO_4) yellow, as shown by μXRD , Fig. 3c. The FTIR spectrum corresponding to the green pigment and drying oil from heterogeneous layer is shown in Fig. 3a layer 1. In this figure, the combination of an aged drying oil and the basic

copper acetate with 1:1 acetate to hydroxide ratio is clearly shown.

However, the presence of a specific compound does not imply that the layer is homogeneous. On the contrary, as mentioned before these green pigments are frequently a mixture of several compounds. The X-ray diffraction pattern obtained shows also the presence of another crystalline basic copper acetate, the one with a 1:3 acetate to hydroxide ratio (Fig. 3c).

Several micro-FTIR spectra obtained from this layer show also the presence of copper oxalates (Fig. 3d). Despite the limitations of the sample preparation method used, i.e., a small fragment crushed into a diamond anvil cell—the presence of copper oxalates seems to increase toward the surface. This is also confirmed by X-ray diffraction analysis.

Finally, in one of the FTIR spectra from the same layer, the OH-stretching vibrations absorption bands characteristic of basic copper chlorides are also determined (Fig. 3e). Some chlorine is detected and concentrated in some few points visible in the μXRF map shown in Fig. 3b. This scattered presence reinforces the hypothesis that, in this case, the basic copper chlorides are formed due to the reaction of the copper compounds with the atmosphere through the cracks present in the paint [26]. Unfortunately, the use of a chlorine containing epoxy resin to embed the sample in this case hinders the identification of superficial chlorine.

The second example presented corresponds to an altarpiece painted by Bernat Martorell, from the second quarter of the fifteenth century. In this case, the overall technique used was egg tempera [2, 4]. Bernat Martorell was already a



Fig. 2 (a) “Sant Joan i Sant Esteve” altarpiece by Honorat Borrassà. (b) Detail from altarpiece. (c) Bright field OM and (d) polarized light OM from polished cross sections of the green sample made by embedding it in an *epoxy resin* afterward polished with diamond paste

well-known artist when he painted this. His paintings show a clear Italian painting influence manifested not only in the style, but also in the use of type II lead-tin yellow pigment (the one containing silicon). The green pigment identified is a mixture of basic copper chlorides and basic copper acetates. In this case, the abundance and relatively homogeneous distribution of chlorine in the whole of the green layer indicates that the basic copper chlorides are part of the original pigment contrarily to what was found in the work by Honorat Borrassà previously mentioned. On the other hand, reaction compounds such as copper carboxylates and copper oxalates are also determined. A small fragment containing the different paint layers was prepared with the aim of obtaining a sequence of diffraction patterns related to the various paint layers (Fig. 4a). Figure 4a shows how both basic copper acetates and basic copper chlorides found in the pictorial layers give very low X-Ray diffraction signals due to their low crystalline nature, and especially when compared

to the other crystalline substances. Thanks to the use of synchrotron radiation some of the compounds are detected, in particular, the basic copper chlorides. Some green particles were separated from the chromatic layer and deposited on an adhesive foil revealing a basic copper chloride with the structure of atacamite (Fig. 4b).

Jaume Huguet is one of the most important artists of the period who painted during the second half of the fifteenth century. In all, the altarpieces from this painter that we have studied [3]—6 altarpieces, of which two are shown here—a green pigment similar to the one identified in the Bernat Martorell paintings was determined. However, the yellow pigment used by Jaume Huguet was found to be always the type I lead tin oxide, the same used by his contemporaries. Again, a mixture of basic copper acetates—in this case with a ratio of 1:3 acetates to hydroxides—and basic copper chlorides are found to constitute the green pigment, shown in Fig. 5a.

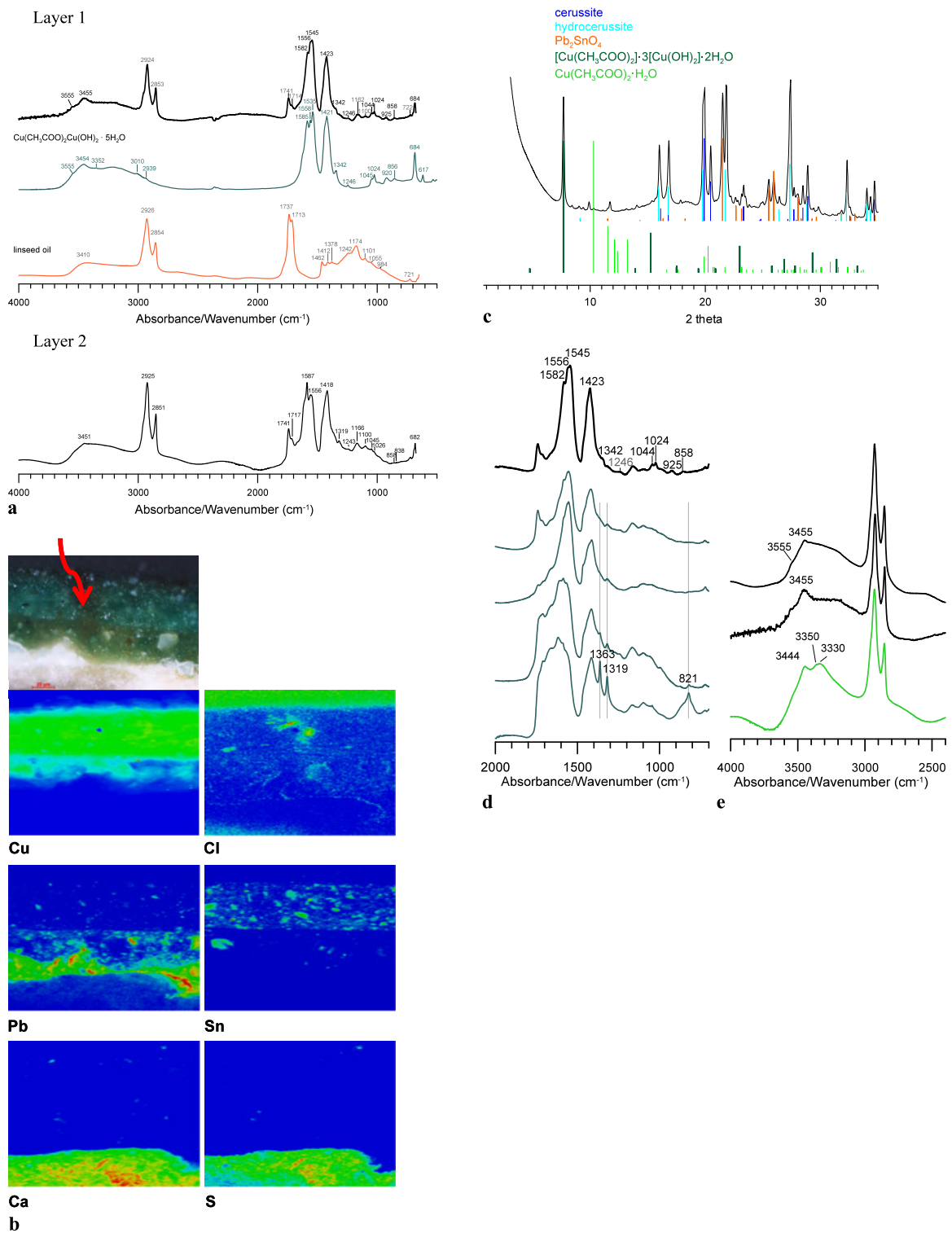
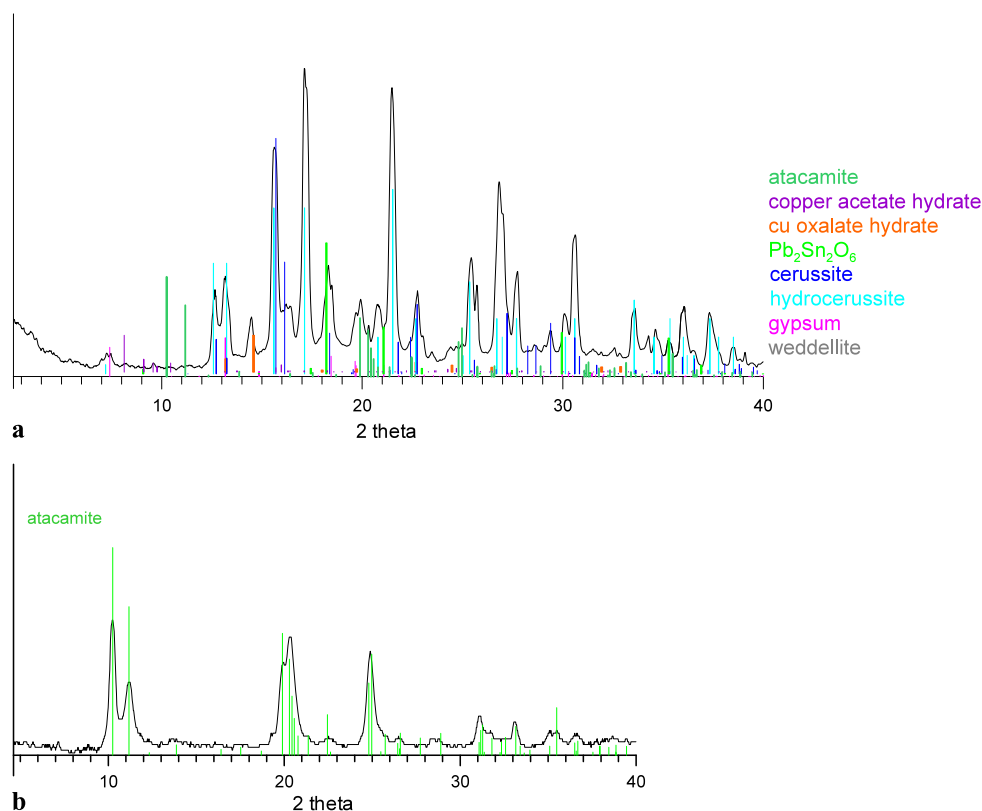


Fig. 3 Analysis using different synchrotron-based microtechniques of a green sample from “Sant Joan i Sant Esteve” altarpiece shown in Fig. 2. **(a)** SR- μ FTIR spectra, corresponding to the green layers—*layer 1 and 2*. The spectrum corresponding to the green layer 1 compared to the drying linseed oil and basic copper acetate reference spectra. 128 scans, 4 cm^{-1} resolution, spot size $12 \times 12 \mu\text{m}$. **(b)** SR- μ XRF, Cu, Cl, Pb, Sn, Ca, and S elemental maps from a polished cross section. SR- μ XRF maps were acquired using energy of exciting beam at 9.05 keV . **(c)** SR- μ XRD pattern from the green paint layer 1. Footprint

$20\text{--}50 \mu\text{m}$, ADSC Q210r CCD detector, 12.7 keV X-rays ($\lambda = 0.98 \text{ \AA}$), transmission geometry. **(d)** Sequence of SR- μ FTIR spectra from the green paint layer 1, from top to bottom is innermost to outermost layer, showing the presence of copper oxalates. 128 scans, 4 cm^{-1} resolution, spot size $12 \times 12 \mu\text{m}$. **(e)** SR- μ FTIR spectra from green paint layer 1, showing the interval that appears the O–H stretching vibration bands. In the green spectrum, these bands are related to basic copper chlorides. 128 scans, 4 cm^{-1} resolution, spot size $12 \times 12 \mu\text{m}$

Fig. 4 SR- μ XRD pattern of a sample from the “Sant Vicenç” altarpiece by Bernat Martorell, (a) from a fragment of a green paint layer sample, (b) from a green particle from the same green layer. Footprint 30–30 μ m, ADSC Q210r CCD detector, 12.7 keV X-rays ($\lambda = 0.98 \text{ \AA}$), transmission geometry



The corresponding μ SR-XRF map (Fig. 5b) of the green paint shows the presence calcium on the surface, i.e., calcium sulphates and oxalates as identified by μ SR-XRD and μ SR-FTIR. Lead tin yellow and lead white are mixed with the green pigment to produce the lighter green layers. Finally, copper is clearly correlated to the chlorine and present in the whole layer emphasizing the presence of basic copper chlorides in the green pigment. It is also necessary to highlight that some of the chlorine determined may be related to the egg yolk—clearly visible in layer 4 (Fig. 5b) made only of lead white and egg yolk. The tendency to form oxalates, in this case of calcium and copper, especially toward the surface is also observed in Fig. 5c, d. The increase in the absorbance $\sim 1320 \text{ cm}^{-1}$ band in the FTIR spectra indicates the presence of calcium oxalates more abundant near the surface.

The last example corresponds to the altarpiece attributed to Pasqual Ortoneda who made use of a tempera technique. Technically, it is of lower quality than the other altarpieces studied here. For example, iron oxides were used instead lead-tin yellow pigments. As in the previous cases, the green pigment is a mixture of copper compounds; in this case, mainly basic copper acetates. The process of alteration of the green pigment may be followed in the sequence of FTIR spectra shown in Fig. 6. In fact, in this altarpiece, the absence of lipids and carboxylates simplifies the identification of the copper alteration compounds. In Fig. 6, we do

observe—apart from the presence of calcium oxalates on the surface—the formation of an intermediate compound between basic copper acetate and a copper oxalate with absorption bands that may be related to a copper formate [27, 28]. This suggests a possible mechanism for the alteration of the copper compounds, which needs to be confirmed by further studies. The absorption bands observed are similar to those outlined for the basic copper (II) formate, $\text{Cu}(\text{HCOO})_2[\text{Cu}(\text{OH})_2]_3$ [28]. However, taking into account the presence of OH groups in the formula, we expected to find $-\text{OH}$ stretching vibration absorption bands in the OH active region of the spectrum. The absence of these bands casts doubt on the specific identification of the compound $[\text{Cu}(\text{HCOO})_2]_x[\text{Cu}(\text{OH})_2]_y \cdot n\text{H}_2\text{O}$; moreover, this OH region is not reported by Ramamurthy et al. [28].

All copper compounds found in the paint layers, such as acetates, hydroxides, basic acetates, basic chlorides, formates, oxalates, and carboxylates, present a range of colors between green and blue.

4 Conclusions

The complementary analytical approach and adequate sample preparation have proved to be fundamental in the study of the green pigments fifteenth century altarpieces. The use

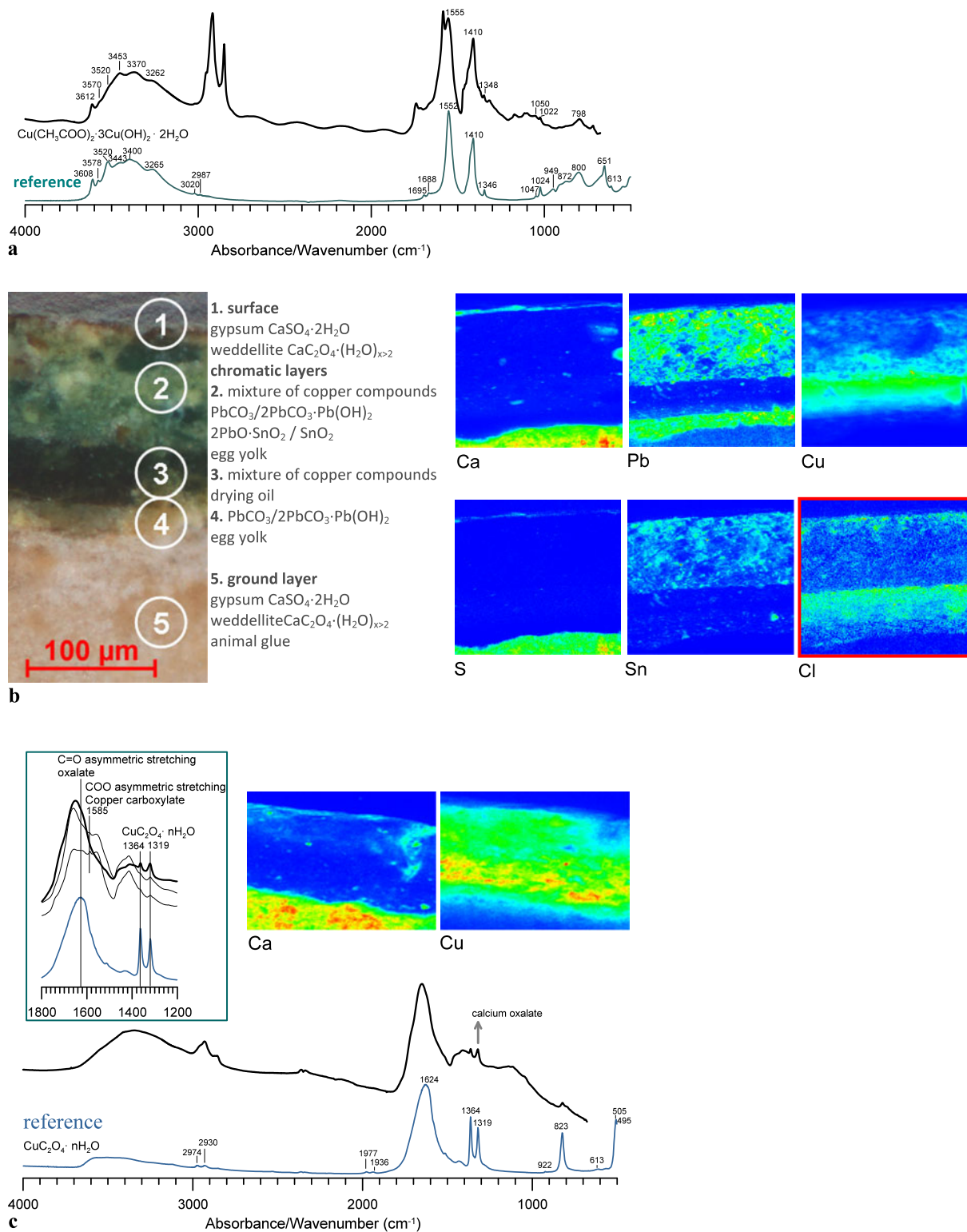


Fig. 5 Analysis using different synchrotron-based microtechniques of green samples from altarpieces by Jaume Huguet (**a**, **b**, and **c** figures correspond to samples from the *Conestable* altarpiece, and **d** figure corresponds to a sample from the *Sant Bernadí i l'Àngel Custodi* altarpiece). (**a**) SR- μ FTIR spectrum corresponding to the green paint compared to the reference spectrum from basic copper acetate. 128 scans, 4 cm^{-1} resolution, spot size $12 \times 12 \mu\text{m}$. (**b**) SR- μ XRF Ca, Pb, Cu, S, Sn, and Cl elemental maps from a polished cross section. SR- μ XRF

maps were acquired using energy of exciting beam at 9.05 keV . (**c**) SR- μ FTIR spectra from the green layer showing the presence of oxalates (128 scans, 4 cm^{-1} resolution, spot size $12 \times 12 \mu\text{m}$). And SR- μ XRF Ca and Cu elemental maps from a polished cross section. SR- μ XRF maps were acquired using energy of exciting beam at 9.05 keV . (**d**) SR- μ XRD pattern from a thin cross section. Footprint $20\text{--}50 \mu\text{m}$, ADSC Q210r CCD detector, 12.7 keV X-rays ($\lambda = 0.98 \text{ \AA}$), transmission geometry

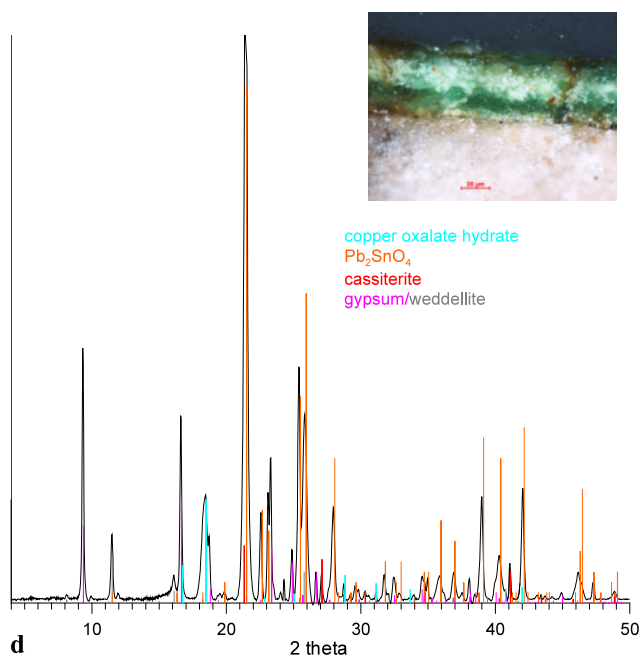


Fig. 5 (Continued)

of synchrotron based microspectroscopy and microdiffraction techniques gave both the micron spatial resolution and the high analytical sensitivity necessary in the analysis.

The green pigments are found to be a mixture of $[Cu(CH_3COO)_2]_x[Cu(OH)_2]_y \cdot nH_2O$ compounds including, in some cases, the presence of $[CuCl_2]_x[Cu(OH)_2]_y \cdot nH_2O$ compounds. However, basic copper chlorides may sometimes result from the weathering of copper acetates/basic copper acetates. The green pigment was often mixed with a drying oil to provide transparency and a glossy appearance to the paint, the use of resins is discarded in the paints from the period and geographical area studied. Malachite was not used as a green pigment. Before the middle of the fifteenth century, the yellow pigment used was a silicon bearing lead tin oxide $Pb(Sn,Si)O_3$ of Italian influence. Later on, a silicon free lead tin oxide $PbSnO_4$ was used due to Flemish influence. When lipids are present in the binder, copper carboxylates are also formed. Copper acetates and copper carboxylates evolve over time to copper oxalates $Cu_2O_4 \cdot nH_2O$. The copper formate identified $[Cu(HCOO)_2]_x[Cu(OH)_2]_y \cdot nH_2O$ could be related to intermediate compounds in the transformation from carboxylates to oxalates. Finally, on the surface and inside the cracks, cal-

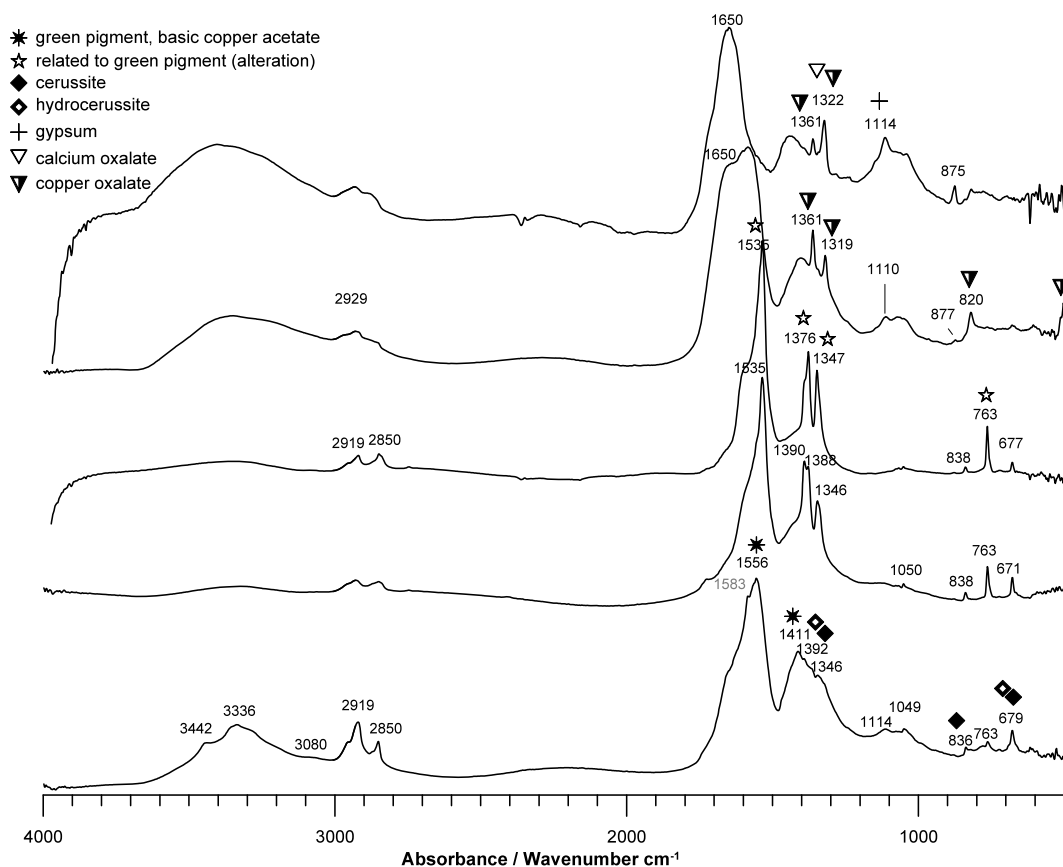


Fig. 6 Sequence of SR- μ FTIR spectra, from a sample from the “Mare de Déu” altarpiece, corresponding to the alteration process the green pigment. 128 scans, 4 cm^{-1} resolution, spot size $15 \times 15\ \mu\text{m}$

cium oxalates and sulphates resulting from the reaction with the environment are also found.

Acknowledgements This research project was funded by: EU (FP7/2007-2013), in the proposal SM6521 (MIRIAM beamline) at Diamond Light Source, EC-805 (beamline ID21) at ESRF; Spanish CRG, under grants 16-01-709/16-01-733 (beamline BM16) at ESRF.

N. Salvadó and S. Butí received financial support under MICINN (Spain), grant HAR2009-10790 and under Generalitat de Catalunya, grant 2009SGR01251. T. Pradell received financial support under MICINN (Spain), grant MAT2010-20129-C02-01 and under Generalitat de Catalunya, grant 2009SGR01225.

Part of this work was carried out within the framework of agreements of collaboration between the Universitat Politècnica de Catalunya (UPC) and the “Museu Nacional d’Art de Catalunya” (MNAC) and the “Centre de Restauració de Béns Mobles de Catalunya” (CRBMC). We wish to thank the VINSEUM Museum for their collaboration in the study and for the access given to sampling of the altarpiece.

References

1. G. Van der Snickt, C. Miliani, K. Janssens, B.G. Brunetti, A. Romani, F. Rosi, P. Walter, J. Castaing, W. De Nolf, L. Klaassen, I. Labarque, R. Wittermann, *J. Anal. At. Spectrom.* **26**, 2216 (2011)
2. N. Salvadó, S. Butí, J. Nicholson, A. Labrador, H. Emerich, T. Pradell, Identification of reaction compounds in micrometric layers from 15th century Gothic paintings using combined SR-XRD and SR-FT-IR. *Talanta* **79**(2), 419 (2009)
3. N. Salvadó, T. Pradell, E. Pantos, M.Z. Papiz, J. Molera, M. Seco, M. Vendrell-Saz, *J. Synchrotron Radiat.* **9**, 215 (2002)
4. N. Salvadó, S. Butí, T. Pradell, *Spectrosc. Eur.* **22**(6), 16 (2010)
5. D.A. Scott, *Copper and Bronze: Corrosion, Colorants, Conservation* (Getty Conservation Institute, Los Angeles 2002)
6. N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium* (Elsevier, Amsterdam, 2004)
7. H. Kühn, in *Artists’ Pigments: A Handbook of Their History and Characteristics*, vol. 2, ed. by A. Roy (Oxford University Press, New York, 1993), p. 131
8. A. López-Delgado, E. Cano, J.M. Bastidas, F.A. López, *J. Mater. Sci.* **34**, 5203 (2001)
9. N. Salvadó, S. Butí, F. Ruiz-Quesada, H. Emerich, T. Pradell, *Butll. Mus. Nac. Art Catalunya* **9**, 43 (2008)
10. G. Cinque, M. Frogley, K. Whebe, J. Filik, J. Pijanka, *Synchrotron Radiat. News* **24**, 24 (2011)
11. V.A. Sole, E. Papillon, M. Cotte, P. Walter, J. Susini, *Spectrochim. Acta B* **62**, 63 (2007)
12. M. Kulkarni, M. Baker, D. Greisen, D. Ng, R. Griffin, H. Liang, *Tribol. Lett.* **25**(1), 33 (2007)
13. R. Salhi, Iran. *J. Chem. Chem. Eng.* **24**(3), 29 (2005)
14. G.V. Seguel, B.L. Rivas, C. Novas, *J. Chil. Chem. Soc.* **50**, 1 (2005)
15. S. Švarcová, M. Klementová, P. Bezdička, W. Lasocha, M. Dušek, D. Hradil, *Cryst. Res. Technol.* **46**(10), 1051 (2011)
16. J.M. de la Roja, V.G. Baonza, M. San Andrés, *Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc.* **68**, 1120 (2007)
17. A. Musumeci, R.L. Frost, *Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc.* **67**, 48 (2007)
18. D.C. Pereira, D.L.A. de Faria, R.L. Constantino, *J. Braz. Chem. Soc.* **17**(8), 1651 (2006)
19. T.D. Chaplin, R.J.H. Clark, D.A. Scout, *J. Raman Spectrosc.* **37**, 223 (2006)
20. F. Quilès, A. Burneau, *Vib. Spectrosc.* **16**, 105 (1998)
21. N. Masciocchi, E. Corradi, A. Sironi, G. Moretti, G. Minelli, P. Porta, *J. Solid State Chem.* **131**, 252 (1997)
22. Théophile préte et moine, *Essai sur divers arts*, ed. Charles de l’Escalopier, Paris 1813 (reed. Nogent Le Roi 1996). ISBN 2-85497-009-8
23. M.P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting: Original Texts with English Translations* (Dover, New York, 1999), p. 236
24. K. Castro, A. Sarmiento, I. Martinez-Arkarazo, J.M. Madariaga, L.A. Fernandez, *Anal. Chem.* **80**, 4103 (2008)
25. P. Richardin, V. Mazel, P. Walter, O. Laprévotte, A. Brunelle, *J. Am. Soc. Mass Spectrom.* **22**, 1729 (2011)
26. N. Salvadó, S. Butí, A. Labrador, G. Cinque, H. Emerich, T. Pradell, *Anal. Bional. Chem.* **399**(9), 3041 (2011)
27. P.C.H. Mitchell, R.P. Horoyd, S. Poulston, M. Bowker, S.F. Parker, *J. Chem. Soc. Faraday Trans.* **93**, 2569 (1997)
28. P. Ramamurthy, E.A. Secco, *Can. J. Chem.* **48**, 3510 (1970)